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Temperature dependence of refractive indices in some nonlinear crystals

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Abstract: Temperature tuning of nonlinear optical devices has been attractive in near infrared nonlinear crystals like ADP and $LiNbO_3$. We have been able to analyse the temperature coefficient of refractive indices in CdS, CdSe, $ZnGeP_2$, $CdGeP_2$ and $CuGaS_2$ from a study of the linear expansion coefficient and the temperature coefficient of the lowest energy gap. The latter two factors determine the temperature coefficient of refractive index. The nondispersive values of the coefficient for several related crystals are found out theoretically. Of the above five crystals only CdSe and $ZnGeP_2$ are phase-matchable for certain nonlinear interactions. We have utilized the analysis to determine the temperature dependent phase-matching characteristics of the following two nonlinear devices Optical Parametric Oscillator, and Difference-mixings which were earlier domonstrated at room temperature.

1. Introduction

High power lasers have made possible to detect and utilise the nonlinear phenomena in optical materials Tunable generation of infrared radiation in nonlinear materials involves three-wave nonlinear interactions giving rise to second harmonic generation, parametric oscillation, sum and difference mixings. The widely used tuning method utilises the variation of crystal refractive indices through changes in orientation of the nonlinear crystal. This in turn alters phase-matching condition and hence results in tunable output wavelengths. An alternative method that has been popular in the visible/near infrared nonlinear crystals like ADP and $LiNbO_3$ is to exploit the temperature dependence of refractive indices in such ferroelectric crystals. However, in the case of infrared region no such study has so far been made.

In this paper we undertake for the first time the evaluation of temperature dependence behaviour of tunable lasers using CdSe and $ZnGeP_2$ as nonlinear crystals. After first providing a physical model for interpolation of temperature dependence of refractive indices in a number of binary and ternary diamond-like crystals we devise a method of predicting the temperature coefficient of refractive indices using some physical parameters. Finally the temperature coefficient of a number of unstudied binary crystals are predicted and the temperature dependence of nonlinear devices using CdSe and $ZnGeP_2$ (which are otherwise estab- lished nonlinear crystals) is discussed.

2. Basic theory

Temperature coefficient of refractive indices (dn/dT) in semiconductors is an electronic effect and is the result of two independent physical processes. These are thermal expansion of the crystal and shift of bandedge with temperature (dE_g/dT). Since a rise in temperature causes the density to decrease the thermal expansion has a negative effect in dn/dT. While the latter gives rise to a positive contribution since dE_g/dT negative in such infrared transmitting nonlinear crystals. In diamond-like semiconductors dn/dT is positive always, which means that the former effect is dominated by the latter. Tsay, Bendow and Mitra (1973) (TBM) have given an analytical expression for the thermo-optic coefficient taking appropriately into account of the above two factors :

$$2n\frac{dn}{dT} = 4\pi\chi_e\left(-3\alpha-\frac{2}{E_g}\frac{dE_g}{dT}\frac{E_g^2}{E_g^2-E^2}\right), \tag{1}$$

where χ_e is the electronic susceptibility, E_g is an *average* optical band gap and E is the photon energy. The above expression can be rewritten in terms of normalized wavelength R (where $R = \lambda^2/(\lambda^2-\lambda_g^2)$) as follows :

$$2n\frac{dn}{dT} = K^2\left(-3\alpha R-\frac{2}{E_g}\frac{dE_g}{dT}R^2\right) \tag{2}$$

where K is a constant determined by the electronic plasma frequency (ω_{pe}) of the material and the Phillips Van Vechten energy gap E'_g as

$$K^2 = \hbar^2\omega_{pe}^2/E'^2_g. \tag{3}$$

The dispersion of the thermo-optic coefficient can thus be simply represented by the formula

$$2n\frac{dn}{dT} = AR+BR^2 \tag{4}$$

where the constants A and B are related respectively to the thermal expansion coefficient and the temperature coefficient of the band gap and these may differ for ordinary and extraordinary polarisations when such index data are used.

3. Results and discussion

3.1. *Determination of the constants A and B*

It is not an easy task to determine the constants A and B from a given set of dispersion data of n and dn/dT. The problem lies in the estimation of an appropriate 'average' optical band gap E_g which enters through R. We adopt a least-squares analysis procedure in which the curve is fitted to a set of $n\frac{dn}{dT}-\lambda$

data points for different values of E_g which in turn is varied from the lowest energy gap to the Phillips-Van Vechten (1969) average energy gap E_g'. The optimum fitted curve produced by a certain value of E_g is then used to find the constants A and B. In this way we have fitted the $n\frac{dn}{dT}$—λ curve for the following five anisotropic crystals : CdSe, CdS, $ZnGeP_2$, $CdGeP_2$ and $CuGaS_2$ as shown in Figure 1 for extraordinray refractive indices and the values of the fitted constants A and B are shown in the table 1 along with ZnS, ZnSe and CdTe fitted earlier by Johnston (1977). However, the values shown for CdTe and ZnS are our own and obtained from updated data of Wolfe *et al* (1978) and De Bell *et al* (1978) and the fitted constants agree well with that of Johnston. Table 2 shows the location of this fitted energy gap relative to the lowest and Philips

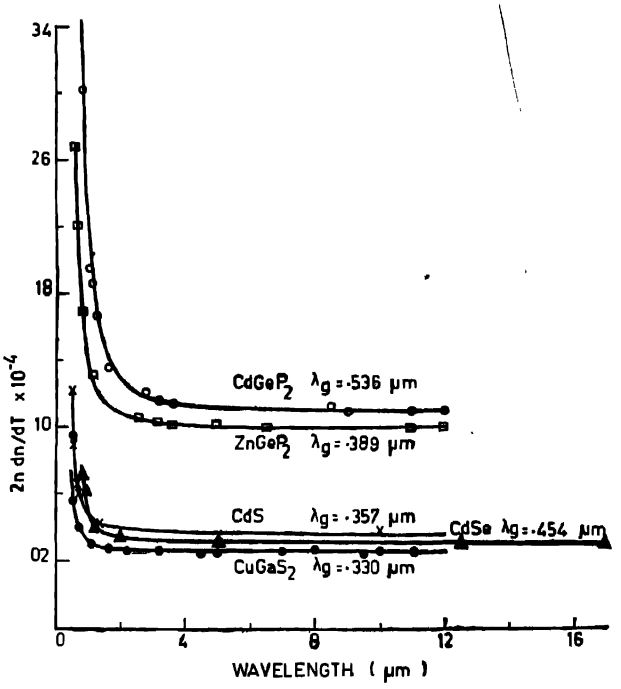

Figure 1. Comparison of experimental data of $2n\frac{pn}{dT}$ vs. λ (extraordinary refractive index for anisotropic crystals) with values computed from parameters in Table 1

Van Vechten energy gaps. (Temperature dependent Sellmeier coefficients were previously formulated in Chalcopyrite crystals (Bhar and Ghosh 1979)).

Table 1. Evaluation of coefficients in dispersion relation

$$2n\frac{dn}{dT} = AE + BE^2 a$$

a All Units are 10^{-5}/°C

Crystal	A	B	$E_g(\mu m)$ (fitted)	Data Sources
ZnSe	−2·29	27·4	·32	Johnston (1977)
ZnS	−2·31	24·13	·25	Wolfe et al (1978)
CdTe	−2·44	50·68	·54	DeBell et al (1978)
CdS	−2·06	37·92	·36	Lisitsa et al (1969) Vitrikhovskii et al (1967), Walsh (1971)
CdSe	−2·36	34·38	·45	Lisitsa et al (1969) Vitrikhovskii et al (1967), Herbst and Byer (1971)
$ZnGeP_2$	−21·12	119·97	·39	Boyd et al (1971a)
$CdGeP_2$	−23·97	133·15	·54	Boyd et al (1972)
$CuGaS_2$	−12·54	38·00	·33	Boyd et al (1971b)

3.2. *Evaluation of the constant K*

From the above fitting constants A and B of the experimental data it is easy to determine the constant K using equations (2) and (4). The experimental values of α and dE_g/dT were used. Since the contribution from the term is negligible compared with that of dE_g/dT, the second term is only used in the calculation. Attempts are also made to determine it from theoretical view point using equation (3). To evaluate the constant K theoretically it is necessary to know the valence electron plasma frequency (ω_{pe}) of the material which is given as

$$(\hbar\omega_{pe})^2 = \left(\frac{4\pi Ne^2}{m}\right)DA \qquad (5)$$

where N is the valence electron density, and D and A are correction factors as was introduced by Levine (1973). The E_g' energy gap for binary crystals was tabulated by Van Vechten (1969). In the case of ternary, an average value for the plasma frequency is first obtained from the corresponding values of the constituent bonds. E_g' for the compound as a whole is then determined from a knowledge of its linear susceptibility through the relation

$$E'^2_g = (\hbar\omega_{pe})^2/4\pi\chi_e \tag{6}$$

The value of K thus obtained using E_g as the average energy gap of Phillips and Van Vechten, is found to agree well with that obtained experimentally (Table 2).

Table 2. Determination of K values of several diamond-like semiconductors

Crystal	Different Energy gap P.V. gap	Fitted gap	Lowest gap	'K' value obtained from Theory (equations 3, 5, and 6)	Experimental (equations 2 and 4)
ZnSe	7·0	3·8	2·6	2·2	1·5
ZnS	7·8	5·0	3·4	2·0	1·4
CdTe	5·8	2·3	1·4	2·3	2·2
CdS	7·1	3·5	2·5	2·0	1·6
CdSe	6·6	2·7	1·9	2·2	1·6
$ZnGeP_2$	5·4	3·2	2·0	3·0	3·1
$CdGeP_2$	5·2	2·3	1·7	3·0	3·4
$CuGaS_2$	7·0	3·8	2·4	2·2	2·5

3.3. *Thermo-optic coefficients of other diamond-like crystals*

The method of determination of K can equally well be extended to other diamond and sphalerite crystals. In those crystals for which d and dE_g/dT values are known, the nondispersive value of dn/dT can be estimated using equation (2). As stated, the contribution from d term is small. In this way we have calculated the same for some crystals and the results are shown in the table 3, which also tabulates some experimental values. Compared to the more sophisticated theory of Tsay *et al* (1973), the agreement of our values with the experiment is encouraging.

Table 3. Prediction of dn/dT for other diamond and sphalerite crystals. The experimental values dn/dT and α are from Tsay *et al* (1973)

Crystal	Temperature coefficient of refractive indices $\times 10^5$ per degree		References
	Predicted	Experimental	
Ge	13·2	13·5	1
Si	28·9	27·6	1
GaAs	18·0	18·8	2
GaP	14·0	11·2	2
InP	22·3	8·4	3
GaSb	28·0	31·1	2
InSb	29·3	47·1	2
InAS	12·3		2
AlP	15·7		2
AlAs	22·7		2
ZnTe	14·4		4

1. Tsay *et al* (1973)
2. Hörig *et al* (1979)
3. American Institute of Physics Handbook 1972
4. Camassel *et al* (1975)

3.4. *Applications in CdSe and $ZnGeP_2$*

As an application of the above procedure of producing interpolated data, we have evaluated refractive indices at different temperatures and analysed the temperature tuning behaviour of tunable devices using CdSe and $ZnGeP_2$ which are the only phase-matchable materials. Temperature tuning of Optical Parametric Oscillation (OPO) and Difference mixing (DC) is only considered.

Because of rather small value of temperature coefficient of birefringence in these crystals the available temperature tuning range is small compared to the ferroelectric crystals. Figure 2 shows the angle tuning curves of 2·36 μm pumped OPO for two temperatures -200°C and $+300$°C which was operated by Davydov *et al* (1972) at room temperature only for a limited turning range. We have earlier (Bhar *et al* 1972) shown that the limited tunable outputs of an OPO can

be further extended by difference-mixing in a second nonlinear crystal. Room temperature difference mixing in CdSe by 1·065 μm pumped OPO was demonstrated by Hanna *et al* (1974). We have used such an OPO for difference-mixing in CdSe crystal for evaluation of phase matching characteristics as a function of temperature. Figure 3 illustrates the tuning curves for such an OPO-DC at two extreme temperatures —200°C and 300°C. Similar results have been

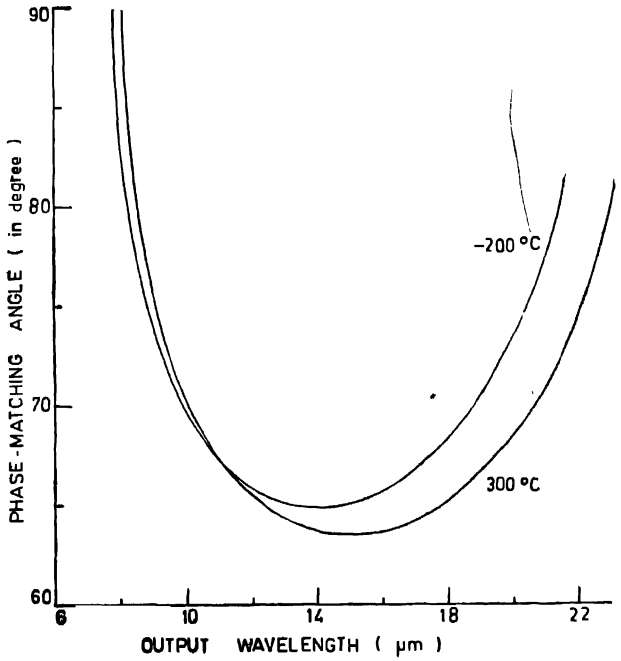

Figure 2. Angular tuning curve for two temperatures—200°C and 300°C for 2.36 μm pumped CdSe OPO

obtained with $ZnGeP_2$ where, however the infrared cut-off wavelength is 13 μm unlike CdSe at 25 μm. It is to be noted that both in CdSe and $ZnGeP_2$ due to smaller temperature coefficient than the ferroelectric crystals the available temperature tuning range is small, which at the same time has the advantage of large temperature stability.

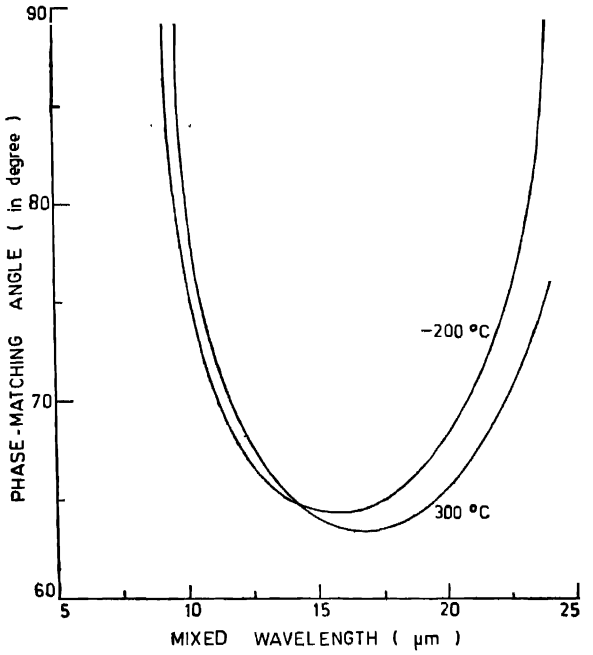

Figure 3. Angular tuning curve for type II a phase-matched CdSe OPO/down-converter at two extreme temperatures —200°C and 300°C using 1.065 μm pump

6. Conclusions

We have analysed the temperature coefficient of refractive indices in five nonlinear crystals to evaluate the temperature tuning characteristics of two phase-matchable materials CdSe and $ZnGeP_2$ for the first time. A method has also been developed to predict the nondispersive value for thermo-optic coefficient.

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References

American Institute of Physics Handbook 1972 3rd ed. (McGrow Hill, New York)
Bhar G C Hanna D C Luther-Davies B and Smith R C 1972 *Opts. Commun.* **6** 323
Bhar G C Ghosh G C 1979 *J. Opt. Soc. Am.* **69** 730
Boyd G D Buehler H A Storz P G 1971a *Appl. Phys. Lett.* **18** 301
Boyd G D Buehler E Storz P G Warnick J H 1972 *IEEEJ Qyan. Electron* QE-8 419
Blyd G D Kasper H M McFee J H 1971b *IEEE J. Quan. Electron.* QE-7 563
Cammassel J et al 1975 *Phy. Rev.* **B 12** 3258
Davydov A A et al 1972 *JETP Lett.* **15** 513
DeBell A G et al 1978 *Annual Meeting Opt. Soc. America*
Hanna et al 1974 *Appl. Phys. Lett.* **25** 142
Herbst R L and Byer R L 1971 *Appl. Phys. Lett.* **19** 527
Herbst R L and Byer R L 1972 *Appl. Phys. Lett.* **21** 189
Horig W et al 1979 *Phys. Stat. Sol* (a) **51** 57
Johnston G T 1977 *Appl. Opt.* **16** 1796
Levine B F 1973 *J. Chem. Phys.* **59** 1463
Lisitsa M P Gudymenko L F Malinko V N and Terekhova S F 1969 *Phys. Stat. Sol.* **31** 389
Miller A Humphreys R G and Chapman B 1975 *J Physique, Colloque* C3 (*Tome* 36) **31.**
Nakau T Nimura H Ozaki Y Kamada S and Hisamatsu T 1978 *Jap. J. Appl. Phys.* **17** 1677
Tsay Y F Bendow B and Mitra S S 1973 *Phy. Rev.* **B8** 2688
Van Vechten J A 1969 *Phys. Rev.* **182** 891
Vitrikhovskii N I Gudymanko L F Mazinchenko A F Malinko V N Pidilisnyi E V and Terekhova S F 1967 *Ukh. Fiz. Zhu.* **12** 790
Walsh T E 1971 *J. Opt. Soc. Am.* **62** 81
Wolfe W L and Korniski R 1978 *Appl. Opts.* **17** 1547